approach.[14] It is thus interesting to revisit CdSe and to study the higher energy excitonic spectra using the same atomistic DD approach. This will examine our theoretical understanding of the system by observing whether agreement with experiment can be obtained without explicitly fitting to the data. This study can also be used as a benchmark for the applicability of the direct diagonalization pseudopotential method and for our detailed understanding of the exciton spectroscopy in a quantum dot.

In the following, we show that, using the direct diagonaliza-

conduction states, covering a E_{ij} range of ~1.4 eV. The resulting $I(E)$'s are shown in Figure 1, where the short vertical negative bars denote the excitonic transition energies $E_{i,j}$ of eq 2, while the positive bars indicate the matrix elements $|\langle \psi_{i,v}|\nabla|\psi_{j,c}\rangle|^2$ for each transition.

We next identify the major transition peaks and assign indices a−i to them (arrows in Figure 1). The assignment is done by considering the line shapes and intensity of the transition peaks and a consistent trend from the small to large quantum dots. Thus, each major peak might contain a few closely spaced small peaks. For the cases where there is no obvious peak position, the center of mass of the major peak is used as the position of the peak. There is some uncertainty in assigning the peak positions, especially in the higher energy part of the spectrum, i.e., peaks f, g, and i. Indeed, had we based our assignments on the spectrum of a single-size dot alone in Figure 1, this uncertainty could have been as large as the separation between the peaks. However, we based our assignments on the observation of the development of peaks as the dot size varies. Consequently, as can be seen in Figure 1, this uncertainty is much reduced. Notice that we have used the full optical spectra to assign the peaks. This is more reliable (especially for the higher energy peaks) than assigning peak positions according to transition energies only.[4]

Before comparing with experiment, we note that the experimental data in Figure 4 of ref 4 contains the effect of phonon replica, exchange splitting, and crystal field splitting, which are not considered in our (or in the k.p) calculations.[18] To subtract these fine-structure effects from the data, we have used the fine structure model of ref 2. On the basis of this model, we calculate from ref 2 a new band gap E_{gap}, which corresponds to the lowest excitation energy E_a in the absence of the exchange splitting and crystal field splitting. The experimental data in Figure 4 of ref 4 is replotted in Figure 2 using this new definition of E_a (see footnote 22 for a more detailed descriptions of this procedure). We also plotted the calculated relative peak energies $E_i - E_a$ ($i = a$ to i) as a function of the effective gap E_a in Figure 2a.

Overall, Figure 2 shows that the present calculation is in very good agreement with experiment. However, not all of the observed transition peaks are accounted for: (1) Our calculation here is limited to dots with $E_{gap} > 2.1$ eV. Dots with smaller band gaps correspond to dot size $\gg$ 1000 atoms that are not calculated here. (2) The energy of the experimental peak j is beyond the energy range of our calculation; thus, there is no corresponding calculated value for it. (3) The experimental peak h is weak and very close to g. Furthermore, it is in the high-energy range of our spectrum, where many small peaks exist. Thus, without analyzing all these details, and without doing an ensemble averages over the different shapes, we do not feel confident to assign such a peak. (4) At the large E_{gap} value (small quantum dot size),(is)-2403,ishepeakhecheath asiz((lculated)-237((erg

the appearance of the crossing remain to be tested by our direct diagonalization method in the future.

In Figure 2b, we have copied the k.p result of ref 4 to compare with the adjusted[22] experimental data. Thus, the same correction is applied to the experimental data as they are compared to the direct diagonalization results and the k.p results. As we can see, the k.p transitions labeled (a), (b) and (d), which were explicitly fitted to the raw experimental data, still agree well with the adjusted[22] experimental results. However, the k.p energy for the other transitions are shifted away from the experimental peaks. Notably, the k.p transition energy (e) is too low for large E_{gap}, and the k.p transition (f) is closer to the experimental peak e than to f. Note that the direct diagonalization pseudopotential results without fitting are closer to

before "-" indicates those angular momenta L's whose sum of $w_{n,L}$ on the heavy hole and light hole bands are larger than 0.1. The L's are in descending order according to their weights. The letter after "-" indicates the highest weight angular momentum L for the split-off band. The last number is an averaged total angular momentum F, calculated as

Here the angular momentum operator $\hat{F}_u = \hat{J}_u + \hat{S}$ ($\hat{S}$ the Dirac spin matrix) applies only to *momeun* , and *momeF*

d point group symmetry. Consequently, the largest degeneracy of the direct diagonalization state is only 2, while in k.p, the degeneracy is (2*momeF*

the final half-integer is the total angular momentum F. We have similarly decomposed our directly diagonalized wave functions $^{a}{}_{i,v}(\mathbf{x})$ into k.p-style envelope functions

where $u_n(\mathbf{x})$ is the nth band *bulk* Bloch function at the Γ point ($\mathbf{k} = 0$), $f_n(\mathbf{r})$ is the corresponding envelope function, and $Y_{L,m}(\iota, \phi)$ is the spherical harmonics of angular momentum L. The total integrated weight of $\sum_{m=-L,L} |f_n^{L,m}(|\mathbf{r}|)|^2$ for each $\{n, L\}$ is denoted as $w_{n,L}$. We have used the heavy hole, light hole, and split-off bands for n, and the total weights on these bands $\sum_{L,n=3-8} w_{n,L}$ is around $\sim$0.9. Figure 4 depicts the dominant weights $w_{n,L}$ of each single-particle state: The capital letter

plot of the DD wave function DG_D2.8. Its envelope function shows orientational preferences in the (110) and (1$\bar{1}$0) directions. On the other hand, the corresponding k.p state 1D_S1/2 is